

Acid Doped Membranes for High Temperature PEMFC

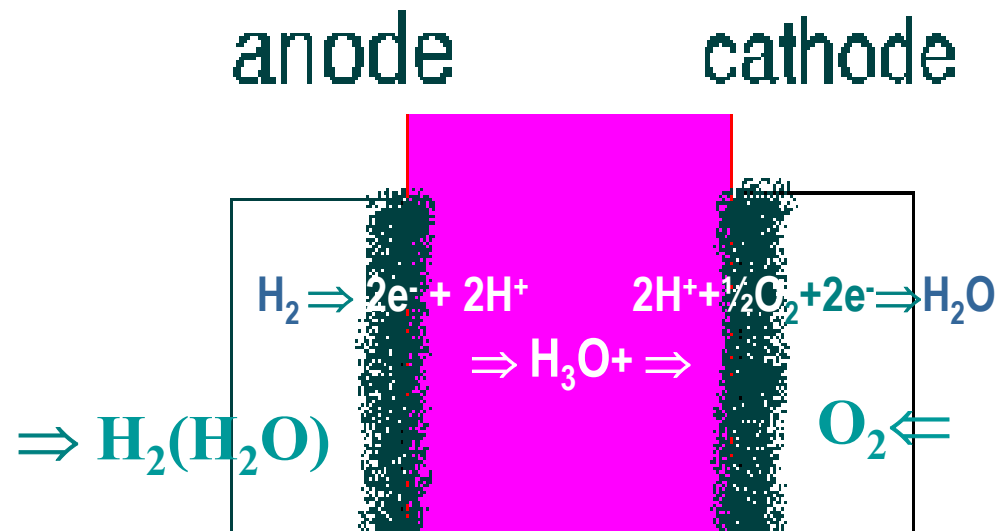
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DOE, May 25, 2004

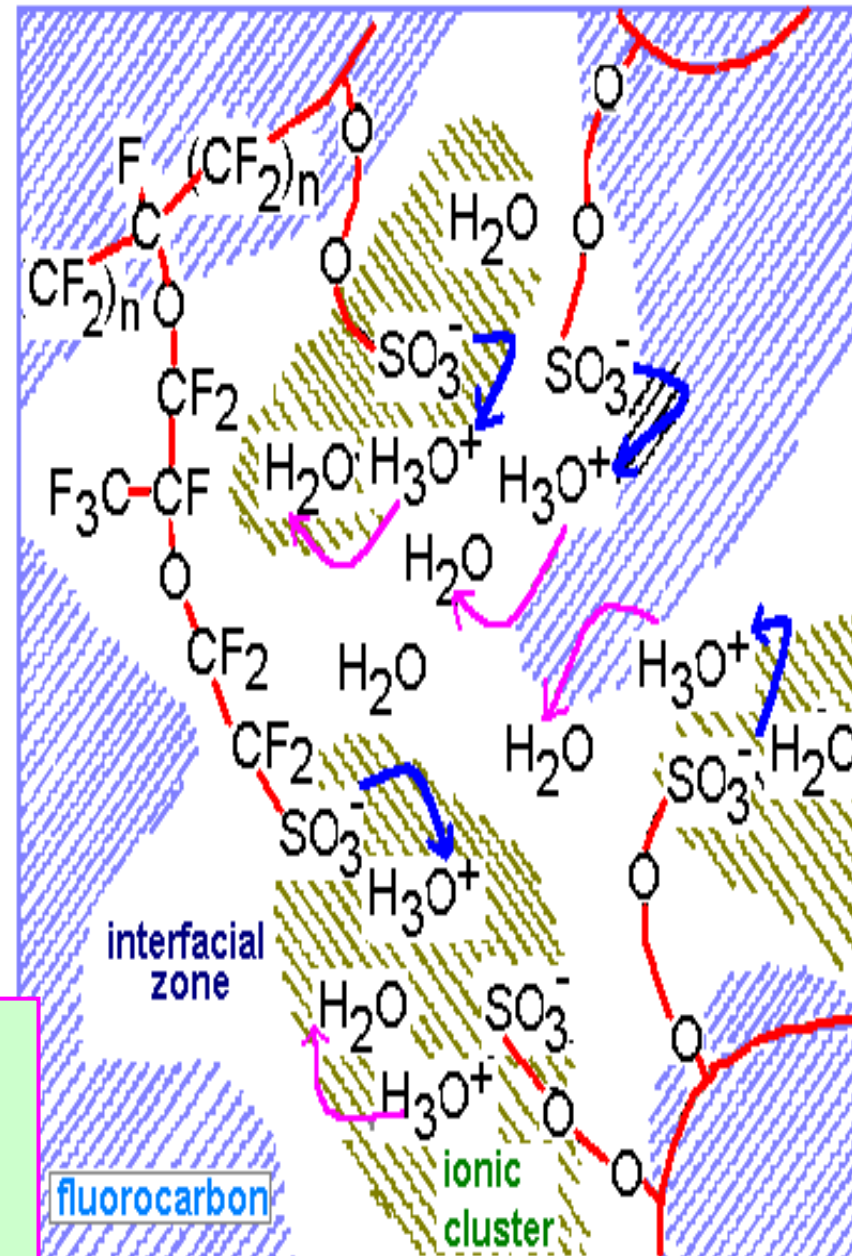
Perfluorinated sulfonic acid membranes (PFSA)

- ◆ Water-dependence of conductivity
- ◆ Water ballance between fluorocarbon and acid groups
- ◆ Electro-osmotic drag of water



As a result:

⇒ Intensive humidification

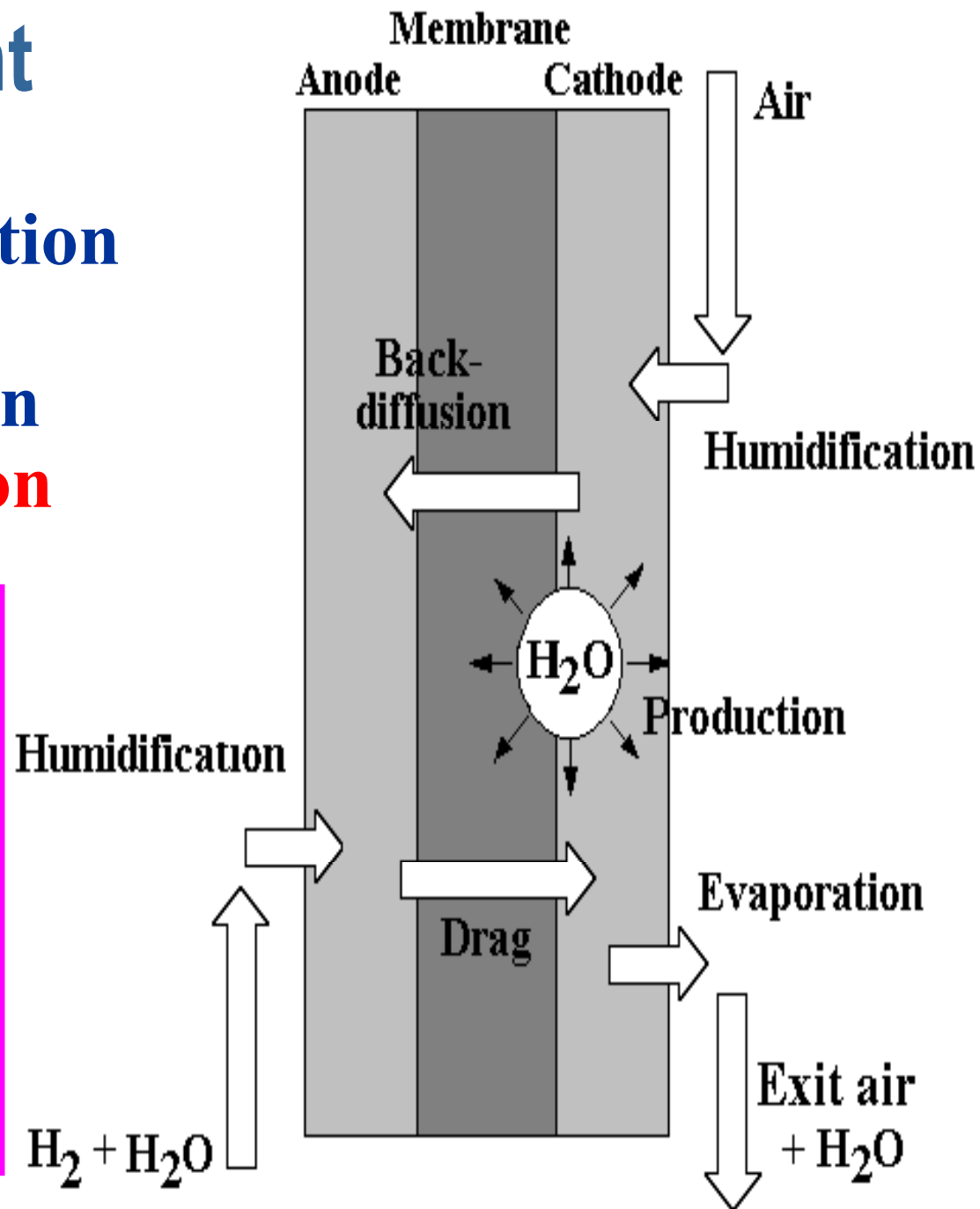


Water management

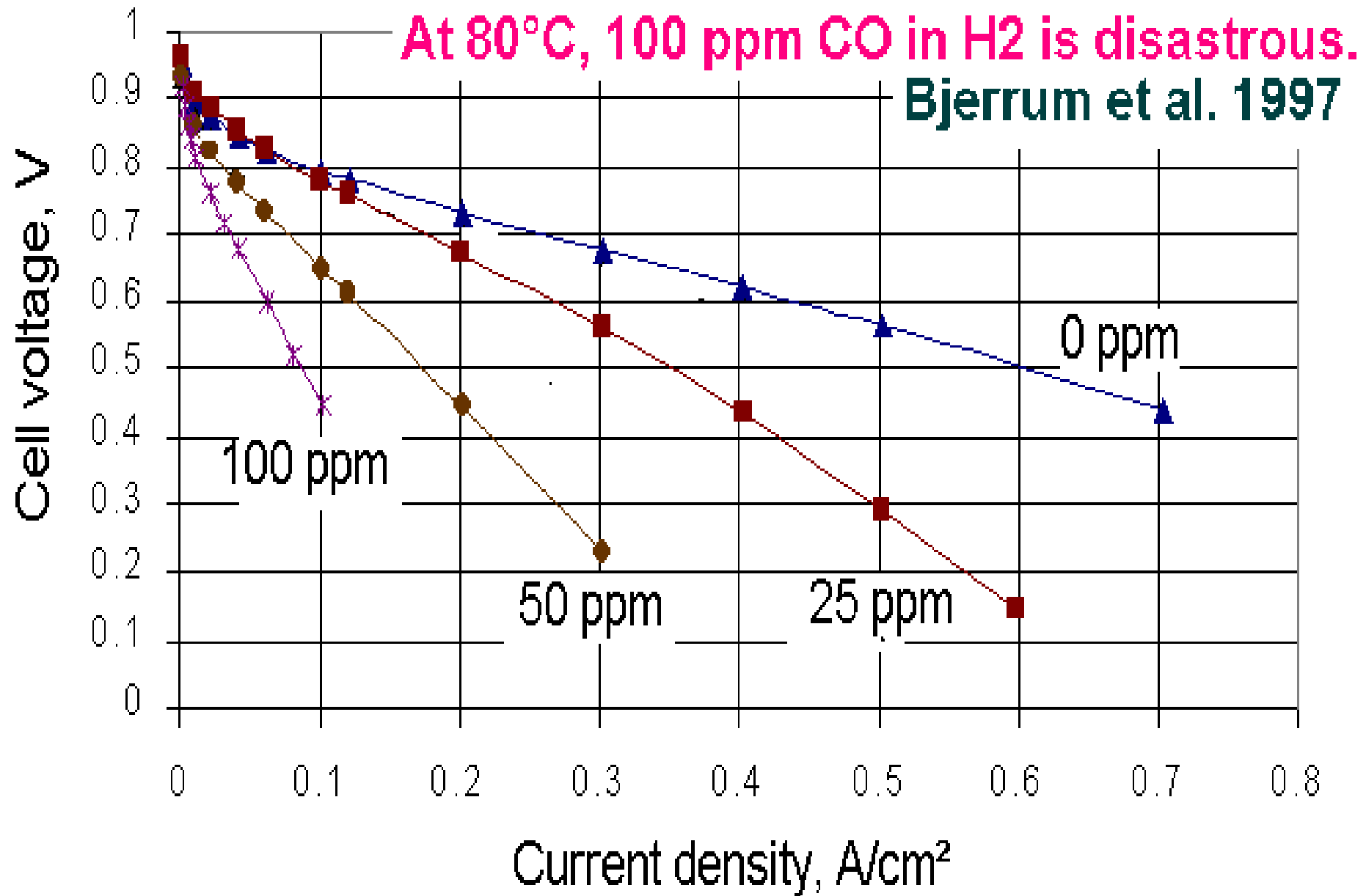
- ◆ Water drag
- ◆ Cathodic production
- ◆ Back diffusion
- ◆ Fuel humidification
- ◆ **Air humidification**

Water removed by evaporation into air

- stack temperature
- air flowrate (λ)
- inlet humidity
- outlet humidity
- pressure



Temperature dependence of CO poisoning



Higher operational temperature.....

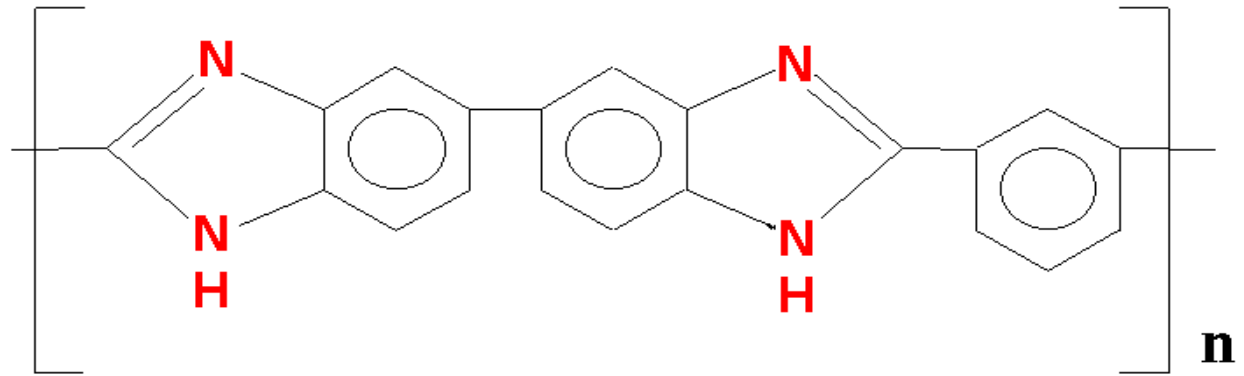
- **Increased catalytic activity**
 - ⇒ Fast electrode kinetics (O_2 reduction and methanol oxidation)
- **High tolerance to fuel impurities**
 - ⇒ Simplified reformer-purification system
(reduced cost, weight, volume, startup / response time...)
- **Avoid two-water-phase operation**
 - ⇒ Simplified stack construction / operation
(water management)
- **Easy thermal management**
 - ⇒ Effective cooling due to temperature gradient
- **Increased value of heat recovery**
 - ⇒ for steam reforming/ H_2 desorption from metal hydride tank

High Temperature Polymers

Polybenzimidazoles

(Poly (2,2'-m-(phenylene)-5,5''-bibenzimidazole (PBI))

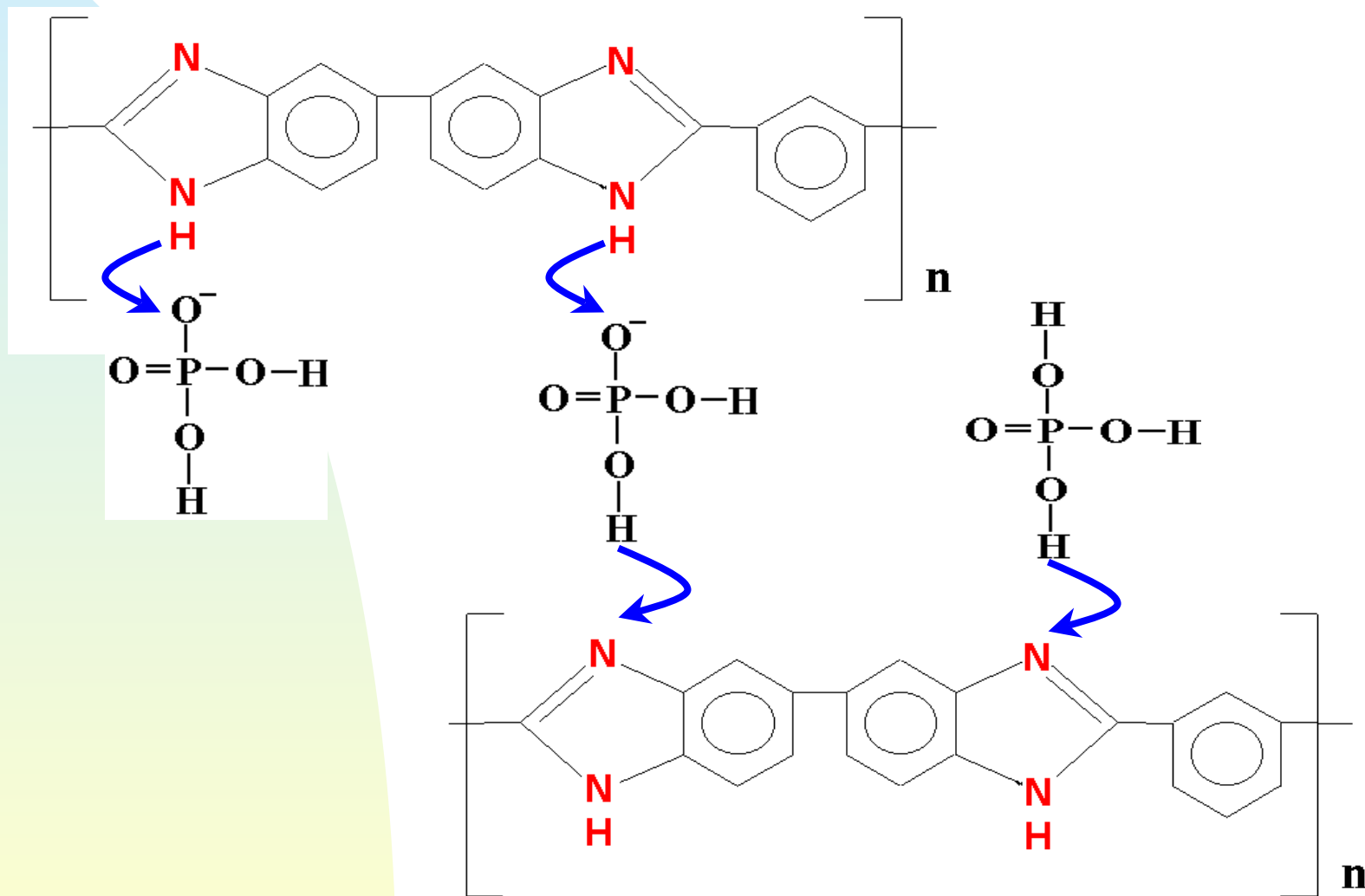
$T_G = 425-435^\circ\text{C}$



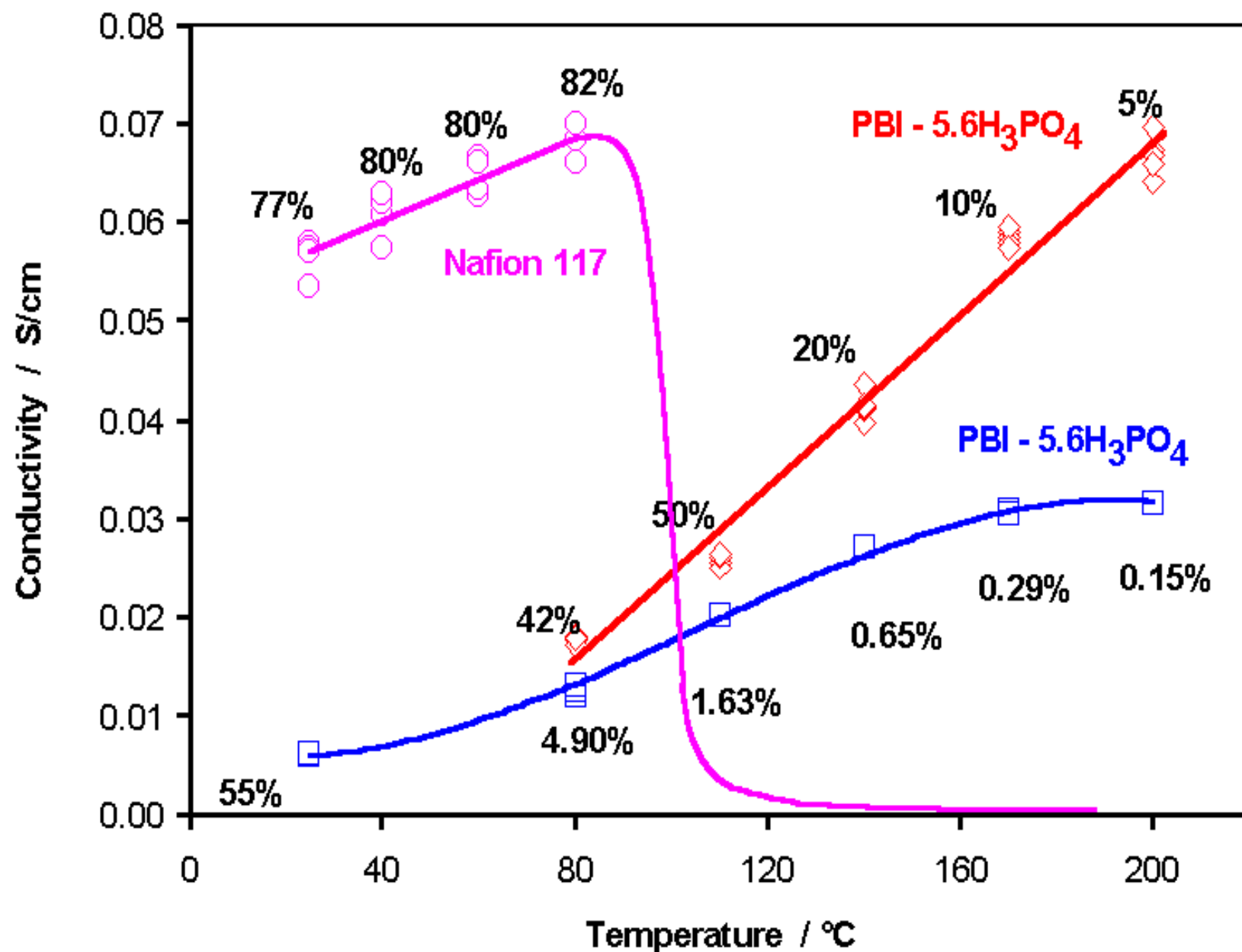
Applications

- ★ As seals, insulator,
- ★ As fibers for protective garments to astronauts, race-car drivers, fire-men ...
- ★ As films & membranes for reverse osmosis and ultra-filtration ...
- ★ Becoming conductive when .. **doped with acids** (Savinell et al, 1995)

When doped with an acid



Conductivity of PBI/ H_3PO_4 membrane



Water-osmotic Drag Coefficient

The molecular number of water dragged by each proton

- **Nafion/H₂O:**

30°C, ≈ 1.4 (Fuller et al., 1992)

1-3, (Zawodzinski et al., 1993)

80°C, ≈ 3 (Bjerrum et al., 1998)

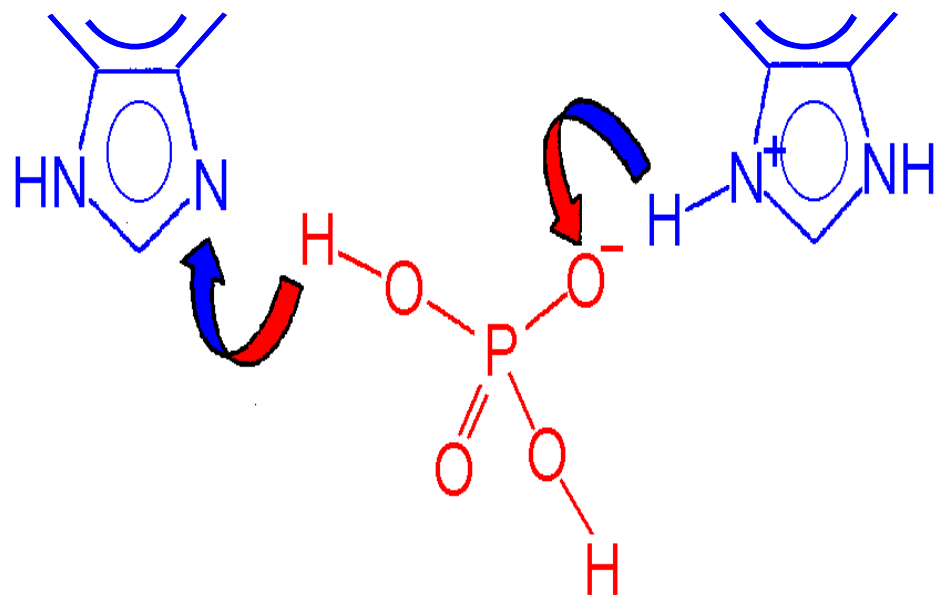
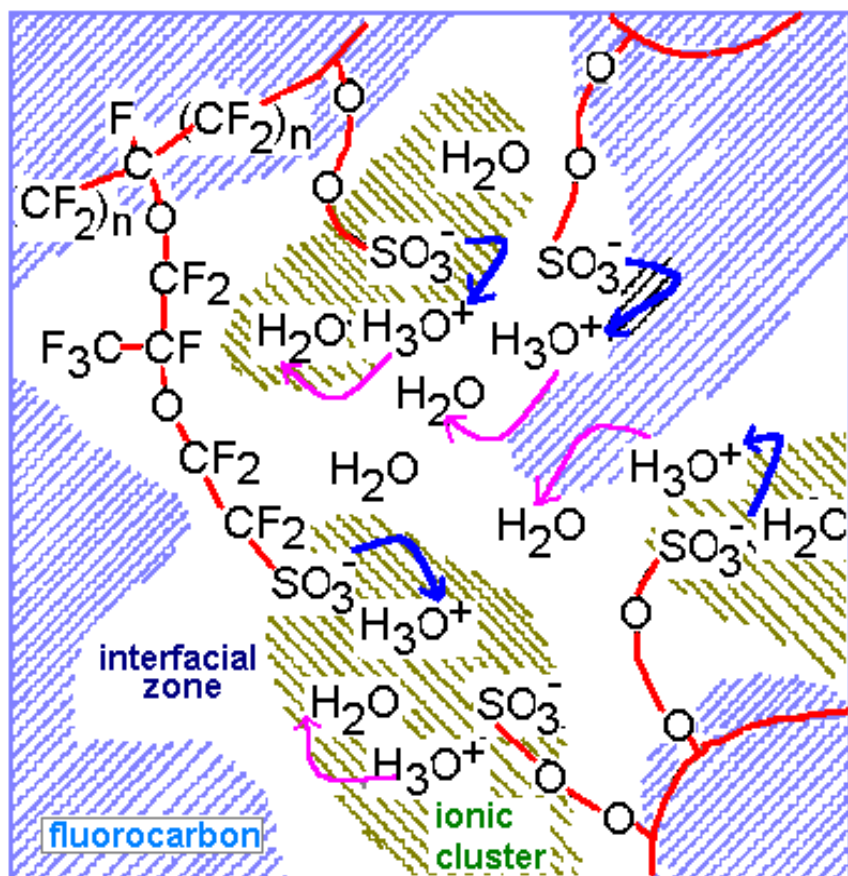
- **Nafion/H₃PO₄:**

125-185°C, 0.2-0.6 (Weng et al., 1996)

- **PBI/H₃PO₄:**

150°C, < 0.03 (Weng et al., 1996)

≈ 0 (Bjerrum et al., 1998)

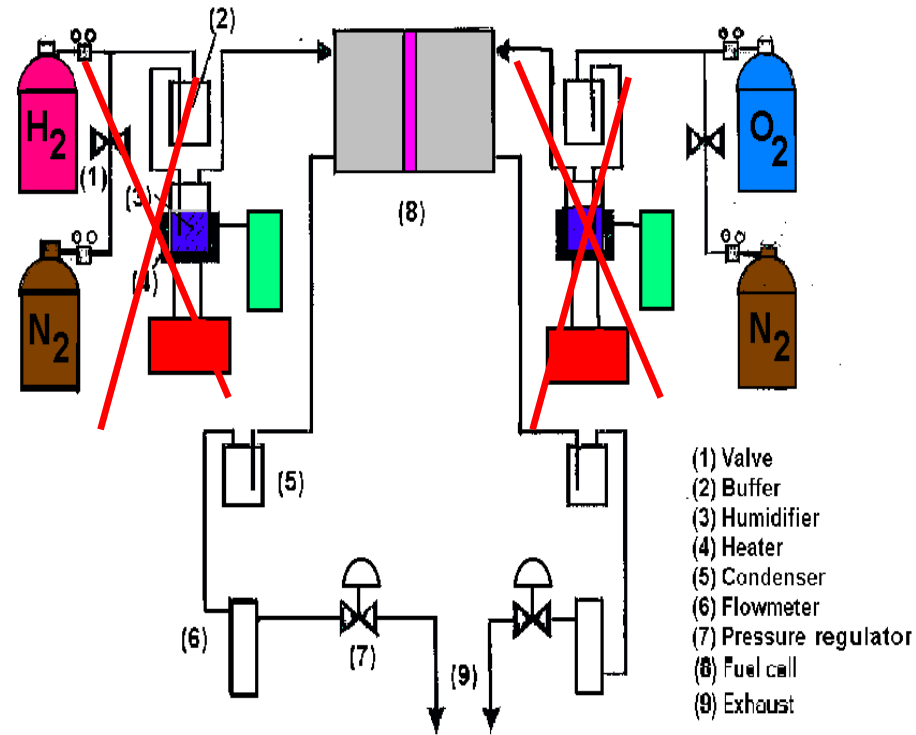
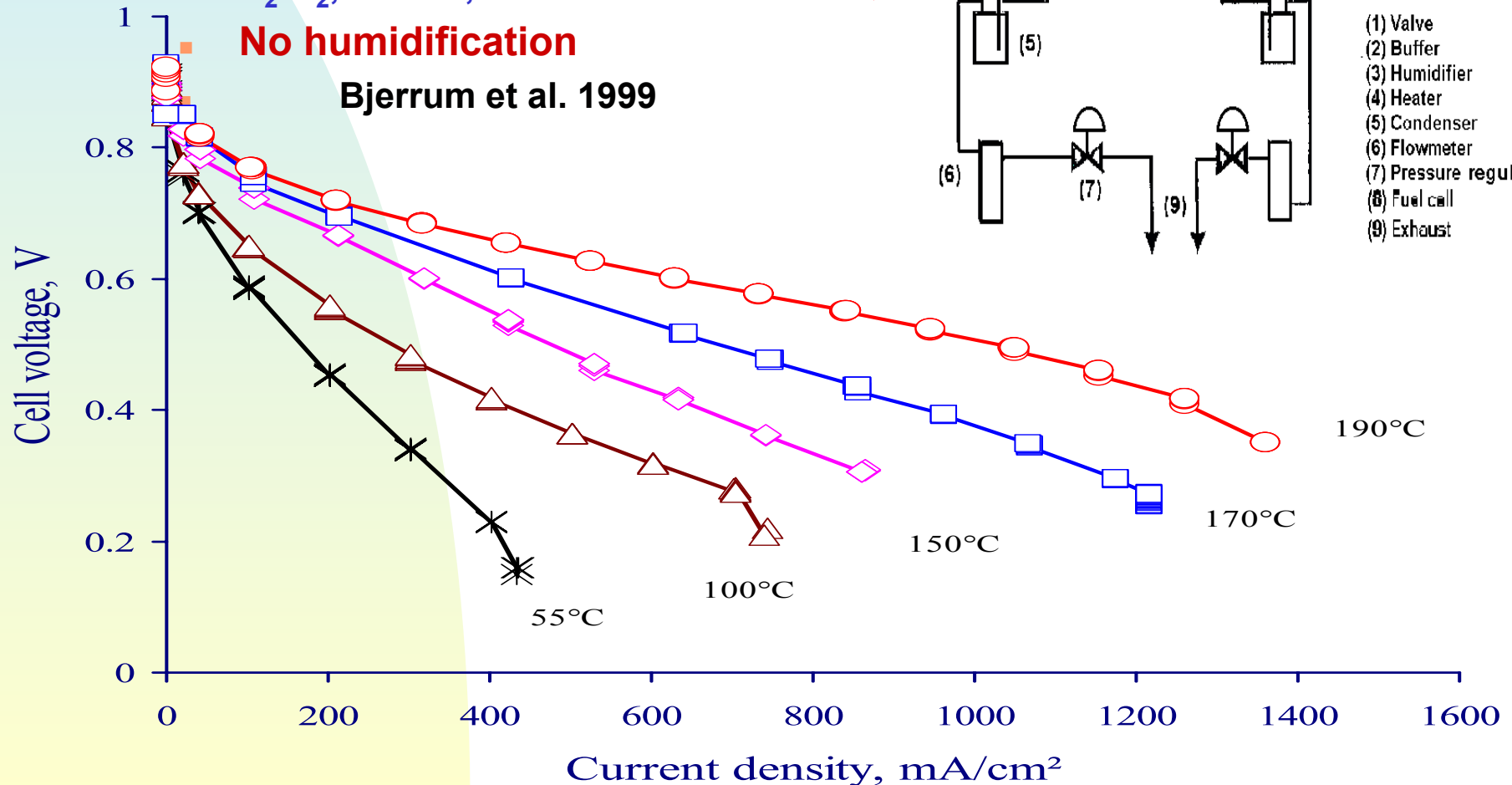


Performance

- different temperatures

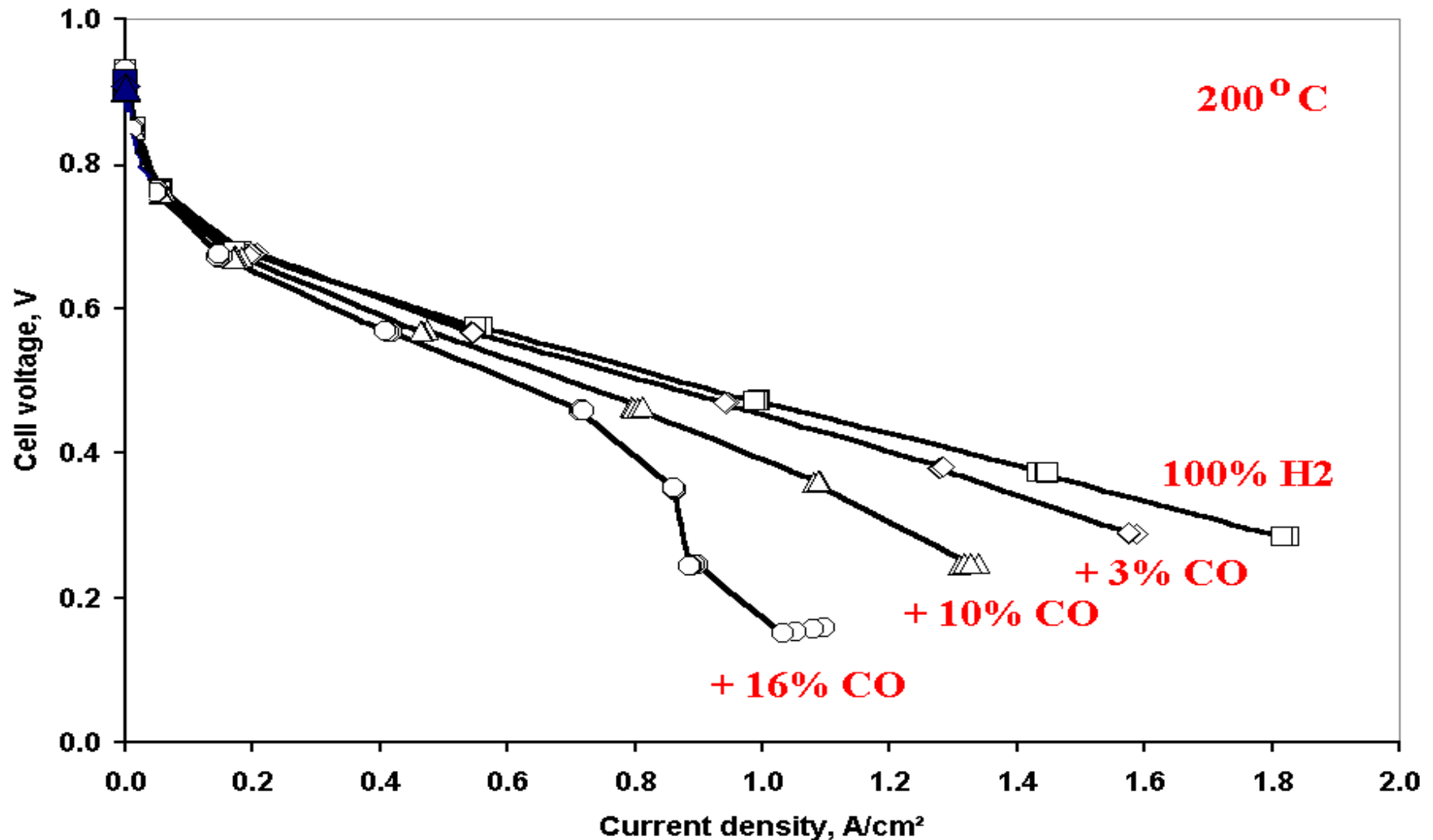
- Electrode, 0.45mgPt/cm²
- PBI/H₃PO₄ membrane
- H₂/O₂, 1/1 bar, 150/150 ml/min
- No humidification**

Bjerrum et al. 1999

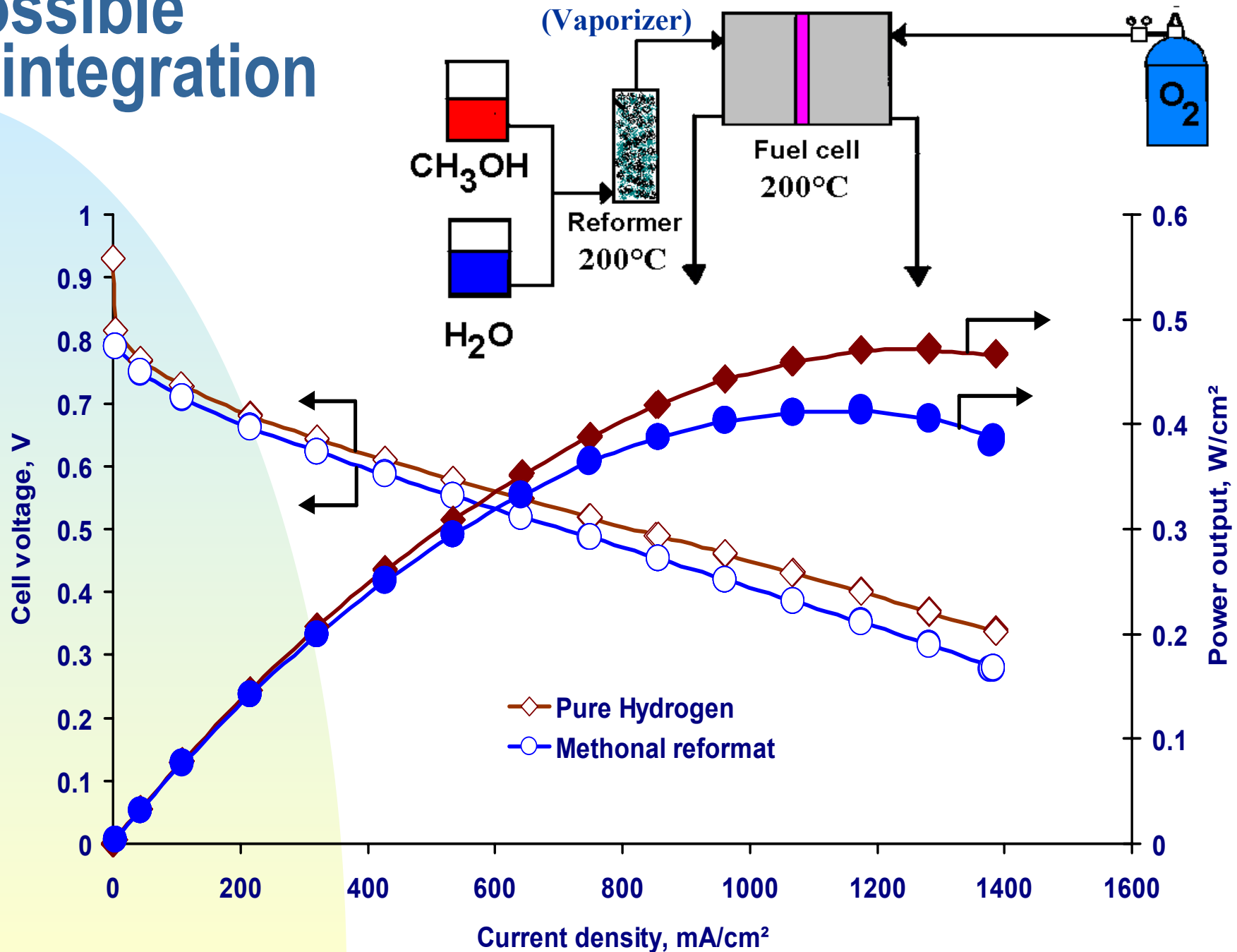


CO Poisoning at high temperatures

At 80°C: Pt/C: 10 ppm CO
Pt-Ru/C: 100 ppm CO
At 200°C: Pt/C: 30,000 ppm CO

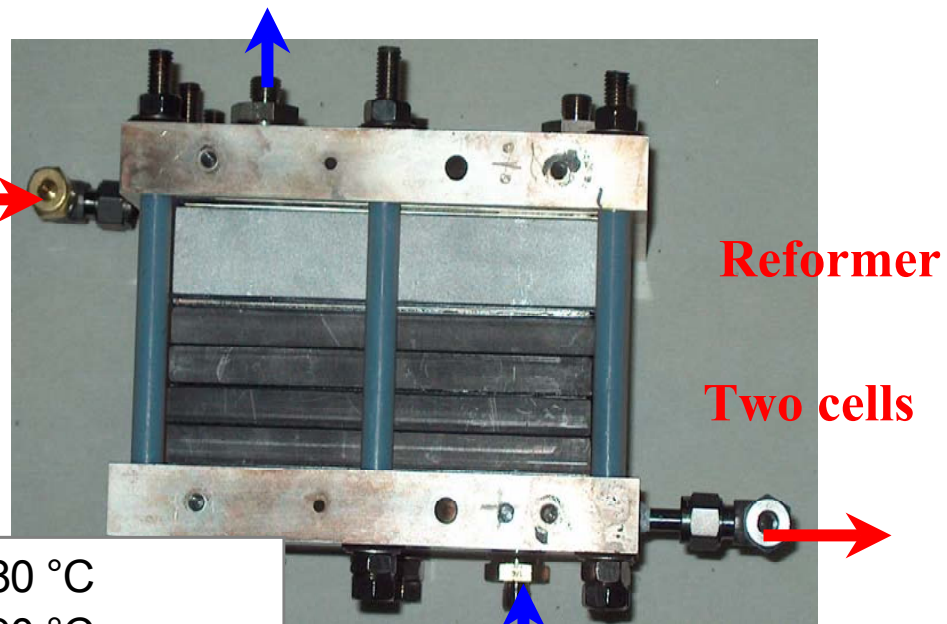


Possible integration

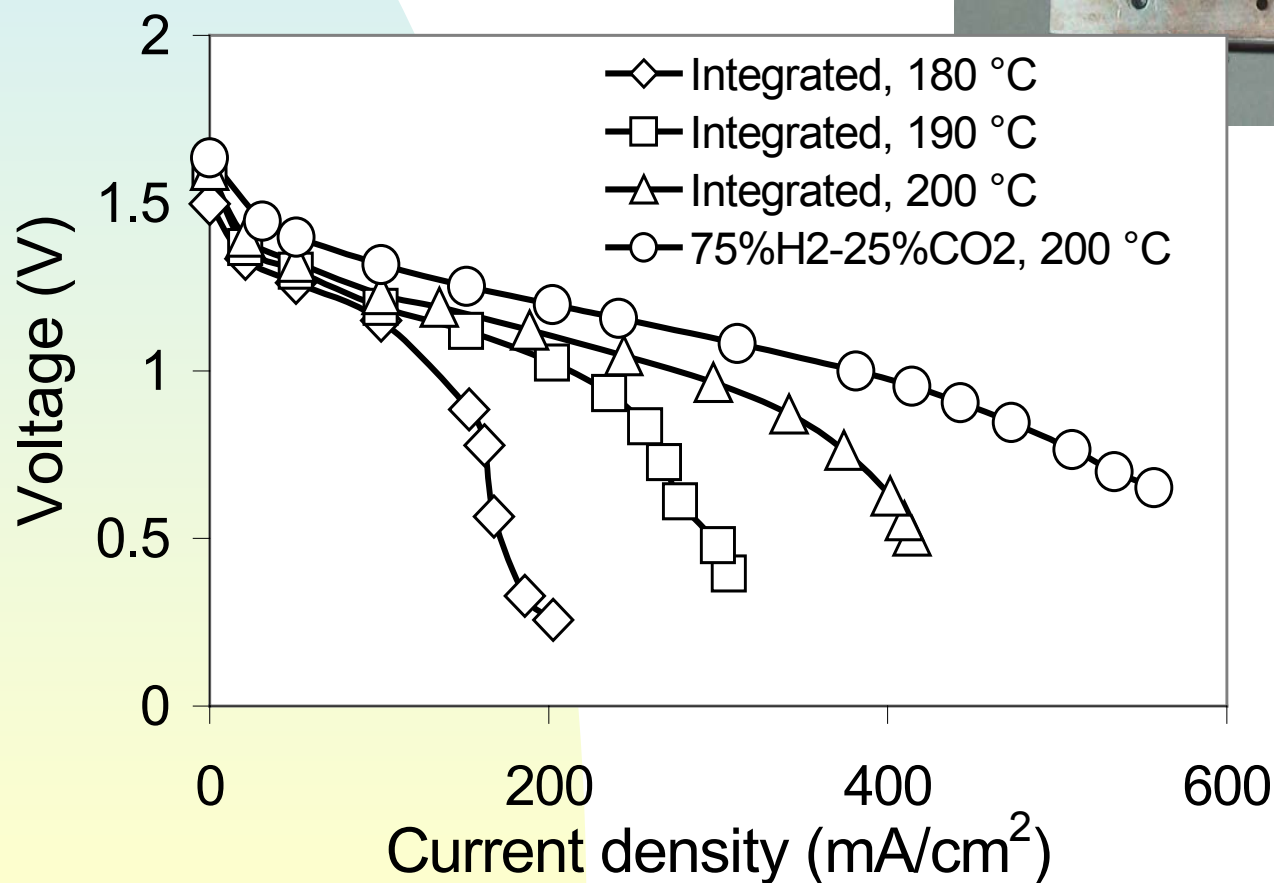


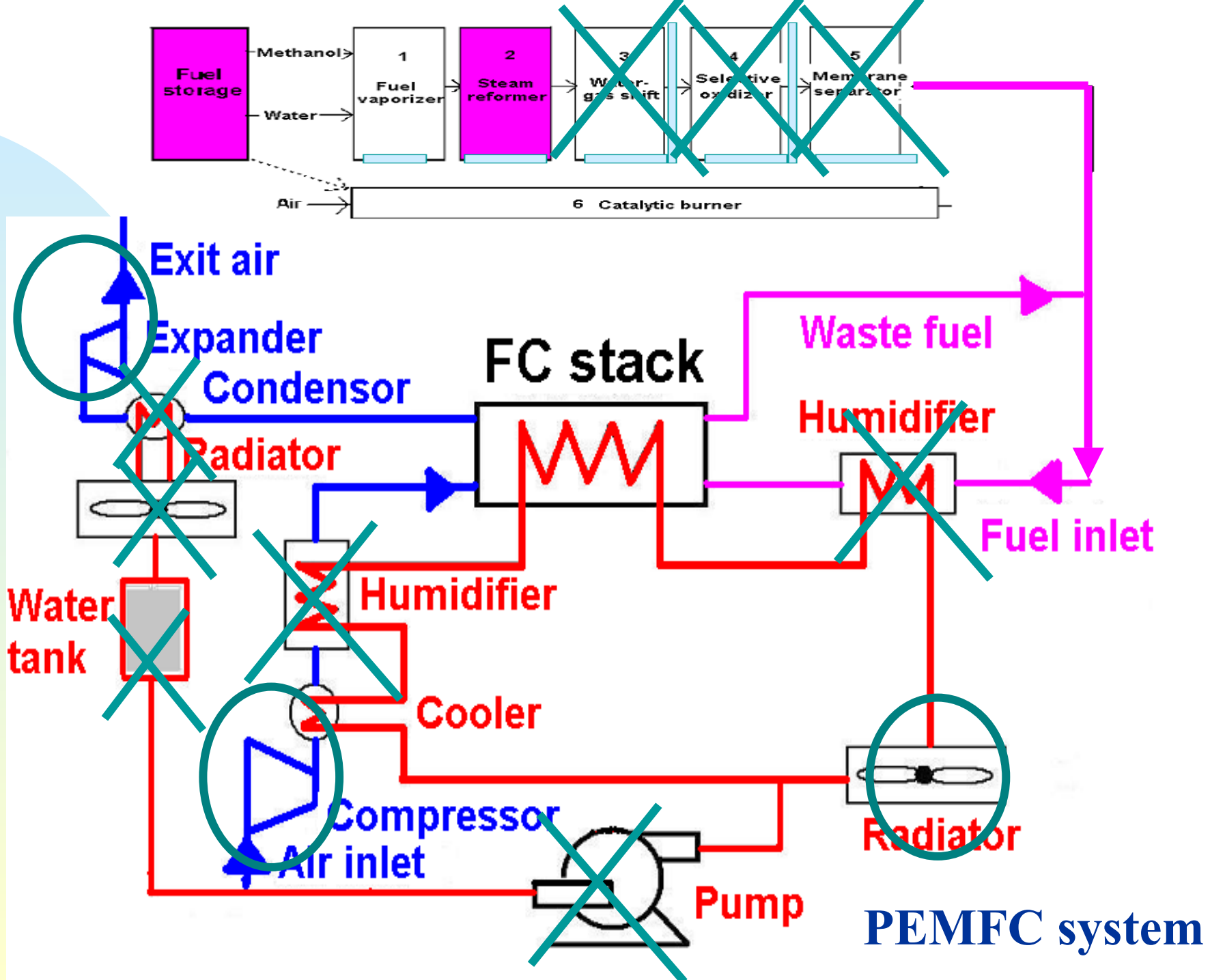
Integration test

CH_3OH
+ H_2O



Air / O_2

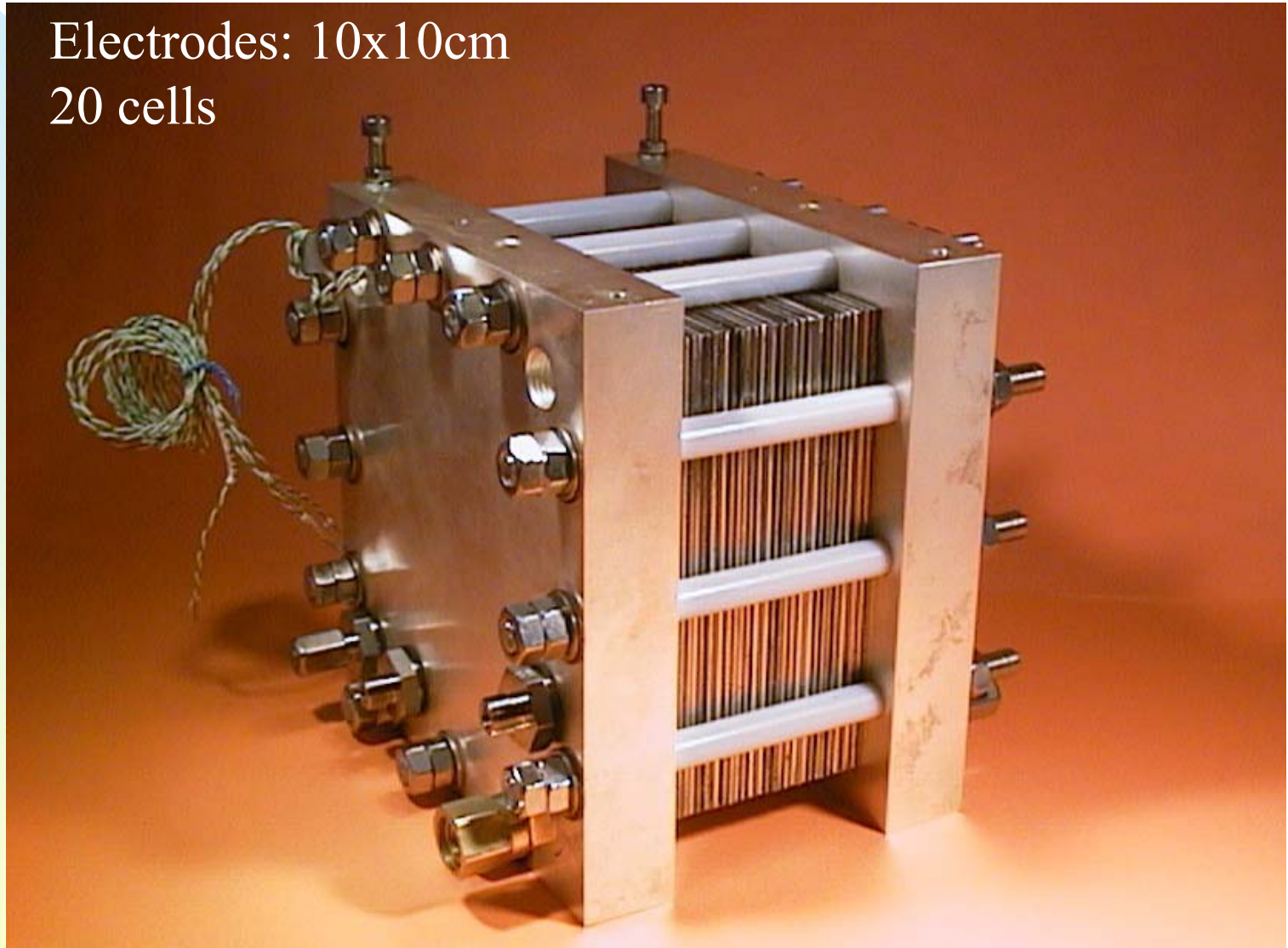




Example of a high temp. PEMFC stack

- developed at Department of Chemistry
Technical University of Denmark

Electrodes: 10x10cm
20 cells



Lifetime – continuous operation

- the 6th Framework Program
Lifetime targets for PEMFC system:

◆ Stationary: >30000 hours
◆ Mobile: >5000 hours

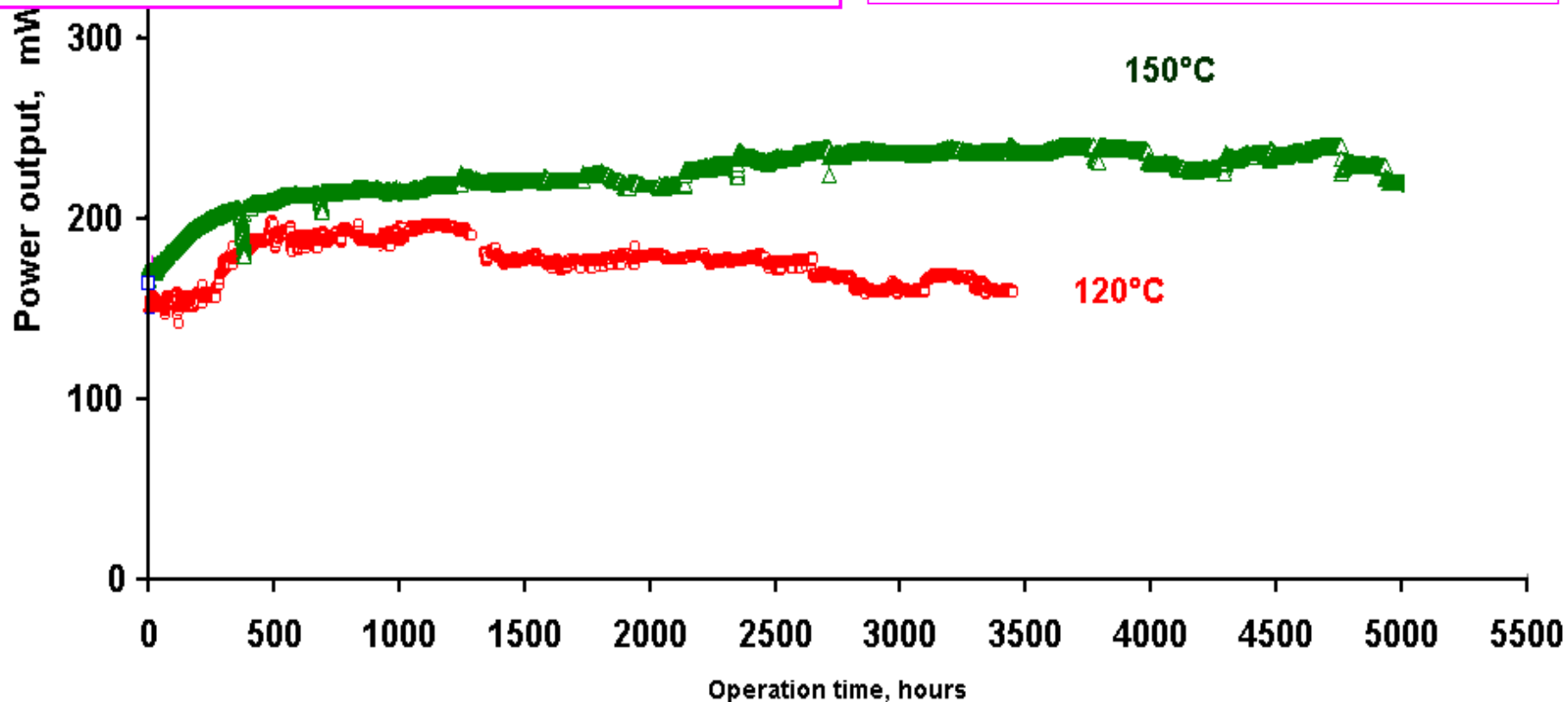
Electrode, 0.4-0.5 mg Pt/cm²

PBI / H₃PO₄ membrane

H₂/O₂, 1 bar/ 1 bar

Operation at constant voltage 0.5V

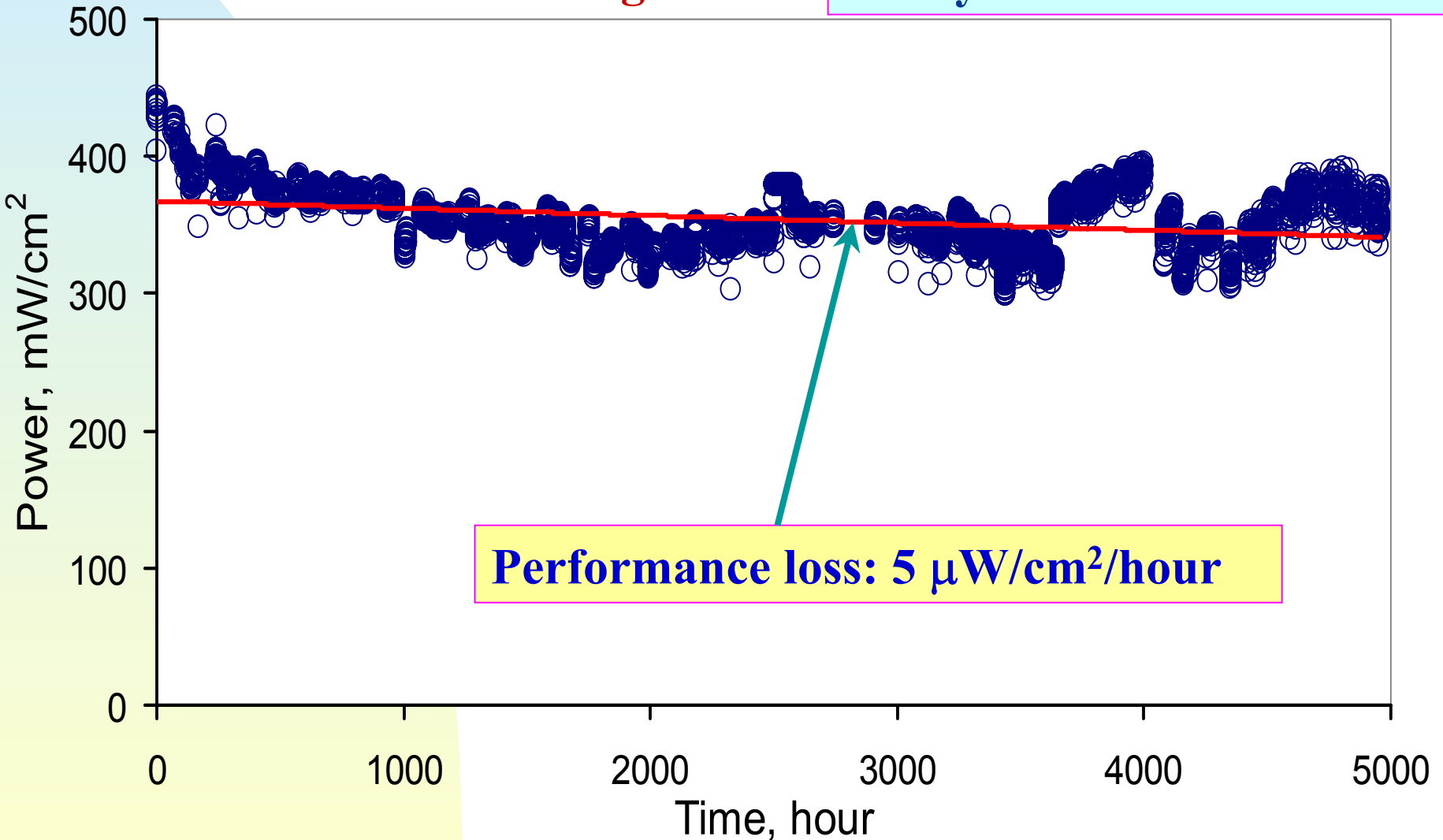
Achieved: 200°C, > 800 hours
180°C, - 1500 hours
150°C, > 5000 hours
120°C, > 3500 hours



Lifetime – thermal cycling

Switch on ca. 7 hours every working days in a period of more than 7 months – still running

Temperature: 150°C
Catalysts: 0.61 mg Pt/cm²
PBI: doping level 5.6
H₂/ O₂ 1/1 bar
140 cycles in 7 months



FURIM project

under the 6th EC framework program

Further improvement of

- Membranes operational 120-200°C**
- Catalysts**
- Electrodes**
- Stack materials**

Demonstration of

- 2 kW stack**
- integrated diesel reformer**
- integrated afterburner**
- feasibility for mobile and stationary applications**

13 partners from 8 countries including USA

Duration: April 2004 – March 2008